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Mechanosynthesis of nanocomposites for chemical interaction with external reagent

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Abstract

The composites mechanically synthesized in immiscible Cu–Bi system, consist of nano-sized particles of copper coated with the bismuth layer 2–3 nm thick. Such mechanocomposites provide an extremely large surface and stabilize this nano-state.

The interaction of mechanocomposites Cu 10 wt.% Bi with liquid gallium–indium and gallium tin eutectics was studied. It was shown that the nano-sized composite provides unusually high reaction rates with liquid eutectic phases.

Keywords: Nanocomposites; Mechanocomposites; Metal system; Mechanical activation

1. Introduction

Mechanochemical synthesis is an efficient way to prepare nanocomposites, and mechanochemical synthesis of nanocomposites can be considered both as a method to create extremely large surface and a way to stabilize the nano-states. It is known that the reactivity of substances increases sharply when their particles reach nanometer size but the problem arises regarding how to prevent the oxidation of these particles in air. In this case, mechanocomposites become almost the only solution to the problem because the particles of the composite powder have micron size and only the outer layer of the micron-sized particles are in contact with the air.

The aim of the present investigation was to study the mechanochemical formation of nanocomposites in immiscible Cu–Bi system and the interaction of these mechanocomposites with liquid gallium eutectics.

2. Experimental

An AGO-2 planetary ball mill was used in the laboratory experiments. In order to avoid oxidation, all experiments were performed in argon medium. X-ray phase analysis was performed by URD-63 diffractometer equipped with graphite monochromator, using Cu Kα radiation. Precise diffraction investigations were performed at the experimental station of Siberian Synchrotron Radiation Center. A detector based on MAR345 imaging plate of Mar research company was used. The distance from the sample to the detector was 400 mm, the dimensions of the beam were 0.4 mm × 0.4 mm, detector resolution was 0.1 mm, diameter of the storage screen was 345 mm. The time of read out of the diffraction patterns with maximal resolution and maximal size did not exceed 2.5 min. Exposure was 7.5 min. So, the process was recorded frame by frame with an interval of 10 min during 24 h.

3. Results and discussion

The enthalpy of mixing in Cu 3 at.% Bi system, calculated by Miedema's method is nearly +1 kJ/mol. According to the equilibrium diagram, this system does not contain intermetallics and has no mutual solubility.

Mechanochemical synthesis was performed in high-energy AGO-2 ball planetary mills using the mode in which the milling bodies get heated to 300–400 °C very rapidly. This mode of mechanical activation provides melting of bismuth on balls, thus, leading to a system composed of a solid and a liquid phase.

X-ray diffraction studies of MA products in the system Cu + 3 at.% Bi show that under the activation conditions applied in our studies, bismuth peaks disappear practically completely within 10 min, copper peaks broaden substantially but do not change their positions (Fig. 1). Nanometric size of composites was revealed by HRTM. X-ray photoelectron spectra provide the evidence that bismuth is on the surface of copper. The thickness if bismuth-enriched layer is 2–3 nm.

In contact with liquid metal (gallium or gallium eutectics), a very thin bismuth layer is likely to pass immediately into the liquid eutectic phase.

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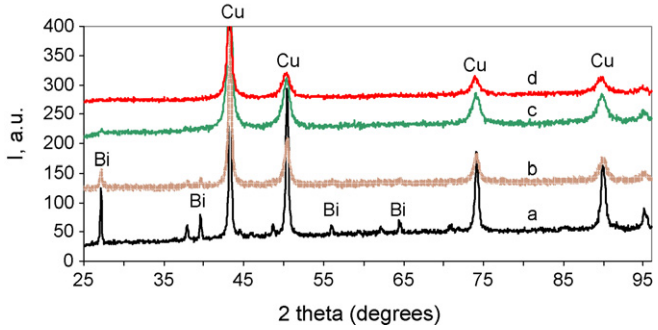

Fig. 1. XRD patterns of mechanically activated mixture of Cu + 10 wt.% Bi. Time of MA: (a) 2 min; (b) 10 min; (c) 15 min; (d) 30 min.

Interaction of mechanochemically synthesized nanocomposites with liquid eutectic was investigated for mixtures (Cu 10 wt.% Bi + Ga 24.5 wt.% In) and (Cu 10 wt.% Bi + Ga 12 wt.% Sn).

Several chemical reactions are possible for the mixture of Cu/Bi and Ga–In eutectic:

$$\text{Cu 10 wt.\% Bi} + \text{Ga 24.5 wt.\% In} \begin{cases} \text{CuGa}_2 + \text{Bi} + \text{In} \\ \text{CuGa}_2 + \text{BiIn}_2 \\ \text{CuGa}_2 + \text{BiIn} + \text{In} \end{cases}$$

The experimental data showed that products of these reactions were $CuGa_2$, $BiIn_2$ and Bi (see Fig. 2). The size of $BiIn_2$ and bismuth crystals is larger than that of $CuGa_2$.

The chemical reaction of Cu 10 wt.% Bi + Ga 12 wt.% Sn → $CuGa_2$ + Bi + Sn was also observed for the composite and the Ga–Sn eutectic (see Fig. 3). Nano-size of composites provides extremely high rates of interaction with liquid eutectic phases (see Fig. 4).

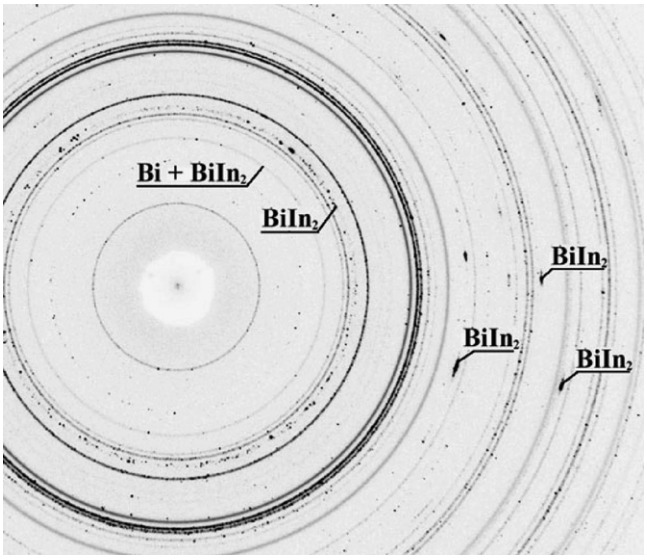

Fig. 2. Diffraction pattern of product of interaction of Cu 10 wt.% Bi with Ga 24.5 wt.% In. Rings represent intermetallic $CuGa_2$.

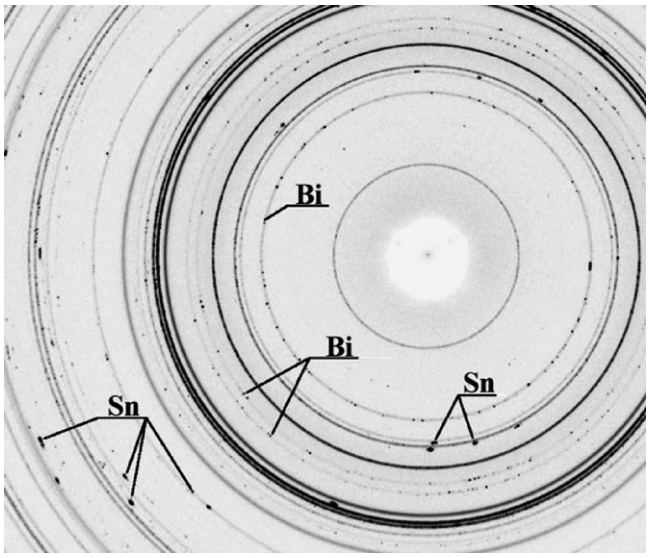

Fig. 3. Diffraction pattern of product of interaction of Cu 10 wt.% Bi and Ga 12 wt.% Sn. Rings represent intermetallic $CuGa_2$.

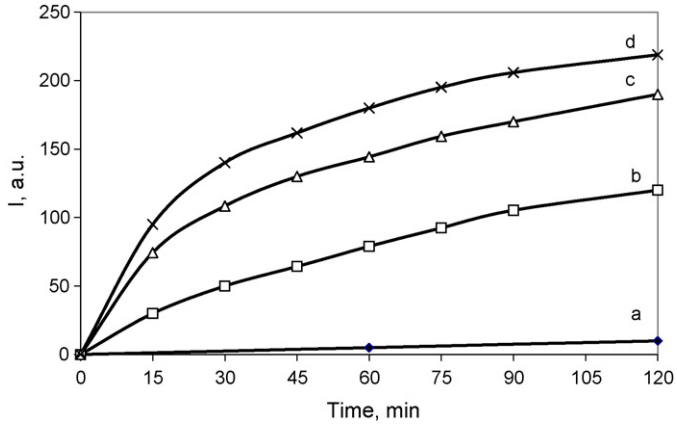

Fig. 4. The dynamics of the growth of $CuGa_2$ phase in the interaction of gallium–tin eutectics with mechanically activated mixture Cu 10 wt.% Bi. Activation time: (a) 0 min; (b) 3 min; (c) 5 min; (d) 10 min.

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